Delayed phase explosion during high-power nanosecond laser ablation of silicon

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(Received 5 December 2001; accepted for publication 7 March 2002)

An important parameter for high-irradiance laser ablation is the ablation crater depth, resulting from the interaction of individual laser pulses on a targeted surface. The crater depth for laser ablation of single-crystal silicon shows a dramatic increase at a laser intensity threshold of approximately 2×10^{10} W/cm^2, above which, large (micron-sized) particulates were observed to eject from the target. We present an analysis of this threshold phenomenon and demonstrate that thermal diffusion and subsequent explosive boiling *after* the completion of the laser pulse is a possible mechanism for the observed dramatic increase of the ablation depth. Calculations based on this delayed phase explosion model provide a satisfactory estimate of the measurements. In addition, we find that the shielding of an expanding mass plasma during laser irradiation has a profound effect on this threshold phenomenon. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1473862]

Laser ablation of solid materials is finding applications in a growing number of areas, such as deposition of metal and dielectric films, and laser ablation chemical analysis.[1] Nevertheless, the fundamental mechanisms underlying laser ablation processes are not fully understood, especially when high-power laser pulses are utilized and superheating of target material occurs. It has been suggested that when the laser irradiance is sufficiently high, explosive boiling[2] is involved such that homogeneous bubble nucleation occurs when the target material reaches $\sim0.9T_{tc}$ (T_{tc} is the thermodynamic critical temperature). As a consequence, the target material makes an abrupt transformation from superheated liquid into a mixture of liquid droplets and vapor, which are then ejected from the target.

Previously, we measured the mass ablation from polished single-crystal silicon with laser irradiance 10^9-10^{11} W/cm^2 (single pulse).[3,4] A neodymium-doped yttrium aluminum garnet (Nd:YAG) laser with 266 nm wavelength and 3 ns pulse duration was focused to ~35 μm diameter spot on the silicon target. The data showed that the ablation depth increased dramatically at the laser irradiance threshold of about 2×10^{10} W/cm^2 (Fig. 1). In measuring the ablation crater depth, a Zygo New View 200 surface structure analyzing system was employed. The system uses scanning white light interferometry to image and measure the microstructures and topography of targets in three dimensions. Below the threshold, the ablation depth increased gradually from 0.6 to 1.5 μm as the laser irradiance increased from 3.0×10^9 to 2.0×10^{10} W/cm^2. At the threshold 2.0×10^{10} W/cm^2, the ablation depth abruptly increased from 1.5 to 6.3 μm, and reached 20 μm at 1.5×10^{11} W/cm^2. Below and above the threshold, a shock wave, which lasts about several tens of ns after the laser pulse, was formed due to the pressure difference between a dense plasma and the ambient. When the laser irradiance exceeds the threshold, there are large size particulates ejected about 300–400 ns after the shock wave. Similar results have been reported by other groups[5,6] using different laser irradiances and pulse durations.

The abrupt increase of the ablation depth at the threshold of 2×10^{10} W/cm^2 was speculated to result from explosive boiling *during* nanosecond laser irradiation, as a laser-induced transparent layer could form when the temperature approached the critical temperature. However, such a transparent layer during pulsed-laser ablation of solid materials was never verified by experiments. In this letter, we demonstrate that thermal diffusion and subsequent explosive boiling *after* the completion of laser irradiation may be a primary source of the measured threshold phenomenon. Calculations of the ablation depth based on a proposed delayed explosive boiling model will be presented. In contrast to previous theoretical investigations of laser-induced phase explosion, we

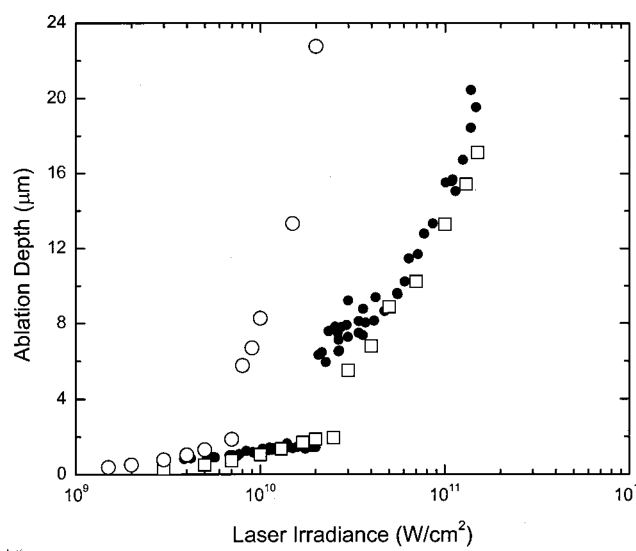

FIG. 1. Comparison of measured ablation depths with the computational data (●: measured ablation depth, □: computational ablation depth with plasma shielding, and ○: computational ablation depth without plasma shielding).

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have included in the calculation the effect of an expanding mass plasma during high-power laser irradiation of the target.

The theory of explosive boiling may be considered from either a thermodynamic or kinetic viewpoint. The former provides a rigorous method to predict the thermodynamic critical temperature, while the latter mechanism models the rate of formation of vapor bubble growth at any temperature. According to the thermodynamic theory of explosive boiling,[7] the liquid begins to be superheated and becomes metastable when it exceeds a temperature limitation of about $0.80T_{\mathrm{tc}}$. Above this temperature, homogeneous bubble nucleation may occur and the "liquid" is essentially a mixture of liquid droplets and vapor which can facilitate explosive boiling. It has been argued that explosive boiling may be a dominant mechanism during the interaction of high-power laser and materials, especially when the laser pulse is sufficiently short (<hundreds of nanoseconds).[8,9]

Although explosive boiling may be an inevitable process when the liquid is superheated, there are limitations according to kinetic theory.[10,11] When the liquid is superheated, homogeneous bubble nucleation occurs and the liquid experiences large density fluctuation. Only if these bubbles reach a critical radius r_c, will they grow spontaneously. Bubbles with a radius less than r_c are likely to collapse, and it takes the bubble a time of τ_c to grow to the critical radius r_c.

Calculations of r_c and τ_c (Ref. 12) using the recoil pressure[13] to approximate the superheated liquid pressure and a power-law relation[14] of surface tension indicate that it would take bubbles about 70 ns to grow to the critical radius of 0.6 μm. Subsequently, the superheated liquid will undergo a transition into a mixture of vapor and liquid droplets, followed by explosive boiling of the liquid–vapor mix. However, our laser pulse duration is only 3 ns; the bubble does not have enough time to reach the critical radius during the laser pulse. As a result, without efficient energy dissipation, the liquid temperature can exceed the critical temperature if the laser irradiance is sufficiently high. The value of τ_c is consistent with our experimental results; in our experiments, micron-sized droplet ejection occurred 300–400 ns after the completion of the laser irradiation.

The thermal penetration depth $x_{\mathrm{th}}=0.969[(k\tau)^{1/2}]$ during a laser pulse of duration τ is much larger than the optical penetration $1/\alpha$ in our case,[15] k is the thermal diffusivity of the liquid silicon, which is about 0.75 cm^2/s, and α is the absorption coefficient. Therefore, the thermal penetration depth is calculated to be about 0.47 μm. The critical diameter of the bubble is $d_c=2r_c$, or 1.2 μm, which is larger than the thermal penetration depth; the bubble can not grow to its critical radius during the laser pulse. Experimental evidence suggests that explosive boiling occurs only if the superheated layer is thick enough.[16]

Martynyuk argued that the rate of homogeneous nucleation,[17] I_n, is numerically significant (i.e., $I_n \gg 1$) only near T_{tc}. As an example, the value for Cs is: $I_n=1$ nucleus/cm^3 s at $T=0.874T_{\mathrm{tc}}$ and $I_n=10^{26}$ nuclei/cm^3 s at $T=0.905T_{\mathrm{tc}}$. The number of homogeneous nuclei which would be generated during the laser pulse is $I_n V^* \tau$, where V^* is the heated volume during the laser pulse, and $V^*=1/4\pi x_{\mathrm{th}} D_{\mathrm{laser}}^2$. D_{laser} is the width of the laser pulse (in our experiments 35 μm), so $V^* \approx 4.5\times10^{-10}$ cm^3. If we take $I_n=10^{26}$ nuclei/cm^3 and $\tau_{\mathrm{hn}}=50$ ns, the homogeneous nuclei generated during the laser pulse equals 5. Therefore, we can not expect that explosive boiling will occur for such a low generation ratio of nuclei.

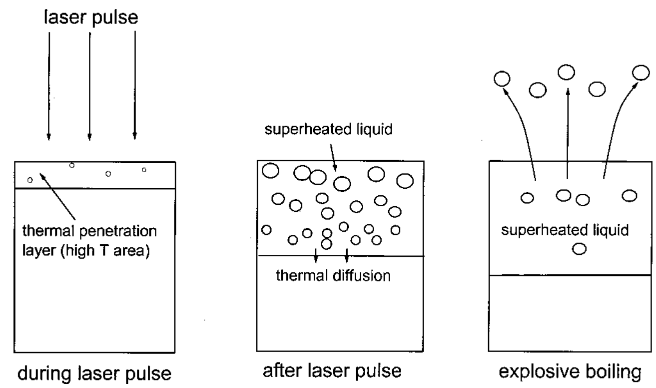

FIG. 2. The processes of laser ablation—explosive boiling.

From this analysis, there are very few bubbles generated near the surface of the target *during* the laser pulse, and those bubbles do not have enough time to grow to a critical size. Therefore, explosive boiling will not occur during the laser pulse. However, without significant bubble formation, a high-temperature layer will form below the target surface during the laser pulse with a depth equal to about the thermal penetration depth. At the same time, the target undergoes normal vaporization from the extreme outer surface. Mass ablation below the laser irradiance threshold 2.0×10^{10} $\mathrm{W/cm}^2$ is generated by this normal vaporization mechanism. The vaporization flux is governed by the Hertz–Knudsen equations, and the velocity of the surface recession can be calculated as,[2]

$$\left.\frac{\partial x}{\partial t}\right|_{x=0}=\beta p_b \frac{m}{\rho}(2\pi m k_B T)^{-1/2} \times \exp\left[\frac{L_{ev} m}{k_B}\left(\frac{1}{T_b}-\frac{1}{T}\right)\right] \mathrm{cm/s}. \tag{1}$$

Here, β is the vaporization coefficient, p_b is the boiling pressure (normally similar to 0.1 MPa), and T_b is the boiling temperature. At high laser irradiance, after the laser pulse is completed, the high-temperature liquid layer will propagate into the target with thermal diffusion. Part of the liquid layer in the target may approach the critical temperature and therefore, new bubbles will emerge inside the superheated liquid, eventually leaving the target (Fig. 2).

A numerical model based on this diffusion-phase explosion mechanism has been established to estimate the depth of laser ablation. Using the heat conduction equation, the distribution of the temperature was calculated according to

$$\rho C \frac{\partial T}{\partial t}=\frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right)+\alpha I_{\mathrm{laser}} \exp(-\alpha x), \tag{2}$$

where T is the temperature, C is the specific heat, and I_{laser} is the laser irradiance which reaches the surface of the silicon target. We include in the model the absorption of laser-generated vapor plasma from the target surface. Such a plasma has been frequently observed during high-power laser ablation of solids. However, it has previously not been included for modeling laser ablation in the explosive boiling regime.

The laser irradiance at the target surface I_{laser} can be written as $I_{\mathrm{laser}}=I_0(t)\exp(-Hk_1)$, where I_0 is the laser irradiance and H is the thickness of the plasma. k_1 is the absorption coefficient of the plasma; in this model, only the inverse Bremsstrahlung process is considered. Details of the model for plasma shielding can be found in Ref. 18, and its validity has been confirmed by comparison with experiments.[19]

The ablation depth due to evaporation was calculated by integrating Eq. (1). During the laser pulse, a high-temperature layer is formed at and beneath the surface of the target, this layer then propagates into the target by thermal diffusion. We regard the liquid whose temperature is larger than $0.85T_{\mathrm{tc}}$ as superheated liquid, and in such a metastable state, homogeneous bubble nucleation will occur.

Ablation for irradiance below threshold is governed by normal evaporation. Ablation for the irradiance larger than the threshold is removed by both normal evaporation and explosive boiling. The ablation depths predicted by this model are compared to experimental data in Fig. 1. The model predicts that the laser irradiance threshold for explosive boiling is about 3×10^{10} W/cm^2, in close agreement with experimental conditions. In our model, the superheated liquid reaches its maximum depth several hundred nanoseconds after the laser pulse is completed, which also agrees with experimental results.

The computational ablation depths without plasma shielding are also given in Fig. 1; plasma shielding plays an important role in determining the laser irradiance threshold for explosive boiling. The effect of plasma shielding can be illustrated by plotting the transmitted laser temporal profile through the plasma (Fig. 3). When the laser irradiance is low, the laser pulse retains its original profile with little attenuation by the plasma. However, when the laser irradiance is larger than 2×10^{10} W/cm^2, the trailing part of the laser pulse is truncated.

In summary, we have analyzed the dramatic ablation depth growth during high-power nanosecond laser ablation of silicon. We developed a model for this threshold phenomenon and demonstrated that thermal diffusion and subsequent explosive boiling *after* the completion of laser irradiation is a potential mechanism. Plasma shielding during laser irradiation was found to have a significant effect on the threshold phenomenon, and our calculations provide a satisfactory estimate of the experimental results. The model developed here should be applicable for a broad range of pulse durations,[20] and we are working both experimentally and theoretically along this direction.

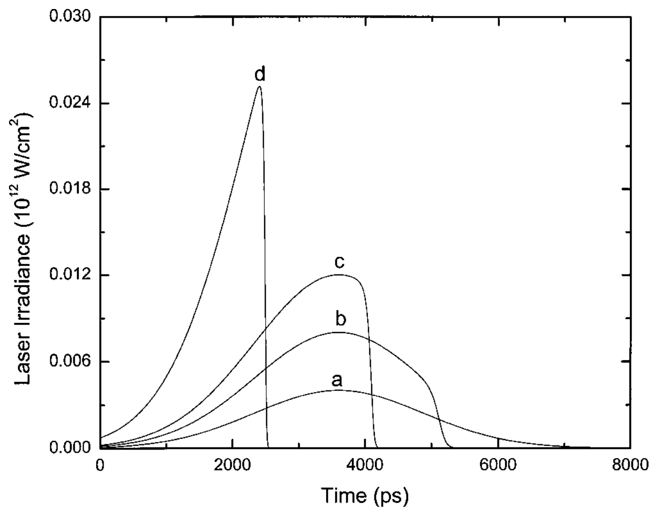

FIG. 3. Temporal profiles of laser irradiance on the target surface for different initial peak laser irradiances, I_{peak}, before the interaction with a mass plasma. The values of I_{peak} are, **a**: 10^{10}, **b**: 2×10^{10}, **c**: 3×10^{10}, and **d**: 1×10^{11} W/cm^2.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract No. DE-AC03-76SF00098. The authors also thank the National Energy Research Scientific Computing Center for providing the supercomputer facilities.

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